

PRODUCT FOR TREATING REINFORCED CONCRETE CONSTRUCTIONSBACKGROUND OF THE INVENTION

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The present invention relates to the construction field. It relates in particular to the treatment of structures made from a cement-based product and having steel rebars, allowing rebar corrosion to be inhibited, preventing the alkali reaction and avoiding the presence of alkalis and sulfates in the structure.

Steel rebars in structures made from concrete are subject to corrosion. The concrete itself may undergo degradation by spalling due to swelling as a result of alkali reactions and to the presence of sulfates or alkalis. This spalling generates cracks that allow water to penetrate into the structure and thus promotes rebar corrosion. This phenomenon is perpetuated until the concrete has been completely destroyed.

Rebar corrosion is promoted by contaminating elements, such as chlorides present in particular in the original sea sand used, owing to the scarcity of river sand, or provided by the salts used for deicing roadways. These contaminants may also be found in sullied demolition-recycling or quarry aggregates, or in products used lately as concrete admixtures (chlorides or sulfates).

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The carbonation of concrete reduces the pH of concrete structures. The rebars, surrounded by concrete, are then no longer protected by its high pH and become sensitive to corrosion. Concrete cracking due to the reactions described above promotes the penetration of water into the structure and consequently corrosion of the rebars.

DESCRIPTION OF THE PRIOR ART

It is known from the document "A study on corrosion inhibitors for concrete applications" by C. Monticelli  
5 et al. to use sodium glycerophosphate for treating concrete structures and protecting their rebars from corrosion.

It is also known, from application WO 93/12052, to use  
10 lithium compounds to inhibit alkali reactions in concrete structures.

Patent US 4 098 614 discloses the use of glycerophosphates, in particular lithium  
15 glycerophosphate for improving the compressive strength of concrete structures.

Patent application WO 02/24973 discloses the use of glycerophosphates for preventing metal corrosion.  
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Patent application WO 01/55052 discloses the use of sodium monofluorophosphate for inhibiting the corrosion of steel rebars of a concrete structure.

25 SUMMARY OF THE INVENTION

The object of the invention is to treat structures in a preventative or curative manner against these phenomena. The invention proposes in particular to  
30 inhibit the corrosion of corroded steel rebars, or of steel rebars that have not yet corroded, and to reinforce the cement mix by preventing the alkali reaction and avoiding the presence of alkalis and sulfates in the structures.

35 These objects are achieved by the use of lithium glycerophosphate for treating structures made of a cement-based product and having steel rebars.

Various ways of implementing methods for treating a structure are defined by claims 2 to 12.

5 A structure according to the invention is defined by claim 13.

#### BRIEF DESCRIPTION OF THE DRAWINGS

10 Figures 1 to 9 show test results that prove the effectiveness of lithium glycerophosphate for the treatment of structures made from a cement-based product and having steel rebars.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

15 It has been found that lithium glycerophosphate has, in addition to a role of inhibiting corrosion of steel rebars held captive in cement-based products, such as concrete and mortar, the ability to protect the  
20 concrete from degradation due to alkali reactions and it has a much greater penetrability into concrete than that of the known inhibitors.

25 The ability of a lithium glycerophosphate to inhibit corrosion on steel that may or may not have already corroded can be observed by impregnating a structure made from a cement-based product containing steel with a lithium glycerophosphate composition. The ability of lithium glycerophosphate to prevent alkali reactions  
30 may be observed at the same time.

The treatment of a concrete structure which has for example undergone degradation due to sulfates and its exposed rebars have undergone corrosion as a result, or  
35 in a concrete that has cracked right to its rebars, will be described below.

Owing to the alkali reaction, the rebars are subject to corrosion. According to the invention, an aqueous

lithium glycerophosphate solution containing 0.1 to 0.5 wt% lithium glycerophosphate is used to treat such structures. This aqueous solution is applied directly to the structure, for example using a brush or roller, 5 or else by spraying using a low-pressure spray device. This solution rapidly impregnates the structure owing to the porosity of the concrete and the ability of the glycerophosphate to penetrate the concrete. The application is made as a single layer or as several 10 layers, allowing between 1 and 2 grams of lithium glycerophosphate per m<sup>2</sup> of concrete to be treated to spread over the surface of the structure.

The object of this application is to obtain, in a 15 region penetrating into the concrete by about 50 mm from the surface where the solution is applied, a lithium glycerophosphate concentration of between 0.001 wt% and 0.5 wt% in the concrete. The rebars that have to be corrosion-inhibited and the concrete that 20 has to be protected from alkali reactions lie within this region. Preferably, the concrete is impregnated with 1.2 grams of lithium glycerophosphate per m<sup>2</sup> of concrete to be treated, so as to achieve a lithium glycerophosphate concentration of 0.01 wt% in the 25 concrete. Other quantities of glycerophosphate may be applied to the structure. The quantity to be impregnated per unit area of structure to be treated depends in particular on the location of the rebars to be treated relative to the application surface, on the 30 porosity of the concrete and on the concentration of contaminants. It will be understood that if the concrete is not very porous or if the rebars are located relatively far from the surface to which the product is applied, or if the concrete is highly 35 contaminated, it is necessary to increase the quantity of lithium glycerophosphate so as to obtain a lithium glycerophosphate concentration near the rebars that is sufficient to inhibit corrosion of the steel and to avoid alkali reactions. Tests, which will be explained

in detail later in the present application, show that, above a lithium glycerophosphate concentration of 0.001 wt% in the concrete, stabilization of the alkalis and sulfates and a very substantial corrosion inhibition effect are already obtained. However, a glycerophosphate concentration of 0.01 wt% in the concrete is preferred, owing to the great heterogeneity of concretes within the same structure.

10 The above treatment may thus be applied, for preventative purposes, to a structure that has not undergone either carbonation, or an alkali reaction, or has not been subjected to other contamination. In particular, it may be applied preventively to sound  
15 structures, in which the rebars have not yet corroded and/or there is not yet any visible cracking.

The lithium glycerophosphate solution used may contain other compounds that also have a corrosion inhibition  
20 function or different functions. In particular, it is possible to use a solution containing components which, in addition to inhibiting corrosion, reinforcing the structures and preventing alkali reactions and the presence of sulfates, allow the solution to be dyed or  
25 pigmented for decorative reasons. Furthermore, the lithium glycerophosphate may be incorporated into paints, for example water-based paints intended to be applied to structures formed from a cement-based product.

30 To inhibit corrosion on the steel making up the rebars exposed to the open air, it is proposed to use a cement-based paint or slurry to which a lithium glycerophosphate has been added. This paint or slurry  
35 is applied to the steel rebars, for example using a brush, a roller, a paint gun or an airless spray gun.

The ability of lithium glycerophosphate to inhibit corrosion on steel may also be observed when it is

incorporated into a cement-based paste intended to immobilize the steel after solidification and in the presence of contaminants.

- 5 To inhibit corrosion on steel that will be contained in a structure made from a cement-based product, it is proposed to use lithium glycerophosphate by itself or in combination with calcium glycerophosphate or other glycerophosphates.

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We will now explain in detail the method for producing a paste of cement-based product for protecting the rebars that will be placed therein and where a risk of degradation exists owing to the presence of  
15 contaminants, such as sulfates, alkalis and chlorides. A concrete is prepared from a cement, for example of the Portland type, sand, aggregate, for example smaller than 15 mm, and water. These products are mixed until a homogeneous paste is obtained. A 1% aqueous lithium  
20 glycerophosphate solution is then added. These products then continue to be mixed until a homogeneous product is obtained. The amount of solution added is such that the concentration by weight of glycerophosphate in the paste is between 0.001% and 0.5%. Preferably, the  
25 amount of solution added is such that the concentration by weight of glycerophosphate in the paste is 0.01%. The concrete paste thus prepared can then be poured, having beforehand positioned the steel rebars intended to reinforce the structure. The rebars may in  
30 particular consist of prestressed cables that are very vulnerable to alkalis.

In the two methods described above, lithium glycerophosphate is used as corrosion inhibitor and as  
35 reinforcement and protection agent against cracking due to sulfates and alkalis. This compound has the advantageous characteristic of being non-toxic - for example it is used in the pharmaceutical industry for its benefits to humans.

We will now present in detail a series of trials carried out in the laboratory and on a construction. These trials demonstrate the benefit of using lithium glycerophosphate for treating structures.

Trial 1:

For this test, a Swiss steel bar of the S500 type was used. This bar was immersed in a 0.1 mol/l sodium nitrate solution and left to corrode until rust appeared on its surface. The electric potential of the steel was measured, right from introducing the bar into the solution, using as reference a silver electrode immersed in a silver chloride solution. The corrosion of the steel lowered its electric potential. After the appearance of rust, lithium glycerophosphate was added to the solution until a 0.1 mol/l concentration of lithium glycerophosphate was obtained. The electric potential of the steel was then observed to increase up to about -160 mV, which meant that the steel had become insensitive to corrosion. This is because it is known that steels whose electric potential is above -200 mV are insensitive to corrosion. Figure 1 shows the curve of the measured electric potential of the steel constituting the bar as a function of time.

Trial 2:

In this trial, the necessary concentrations of various products for achieving a corrosion-inhibiting effect were compared. The products studied were lithium glycerophosphate and other products used in the prior art as corrosion inhibitors. For each product, four solutions having different concentrations, namely 0.001, 0.01, 0.1 and 1 mol/l, were prepared. After having immersed mild steel specimens in each of the above solutions for 28 days, the steel specimens were examined with the naked eye to see whether or not there were traces of corrosion. Table 1 below gives, for each

product, the minimum concentration for preventing the steel from exhibiting any trace of corrosion.

Table 1

Product	Concentration (mol/l)
lithium glycerophosphate	0.001
sodium monofluorophosphate	1.000
diethanolamine	0.100
triethanolamine	0.100
diethanolamine phosphate	0.010
triethanolamine phosphate	0.010
triethanolamine borate	0.100

- 5 It is apparent from this trial that a very low concentration (0.001 mol/l) of lithium glycerophosphate is sufficient to inhibit corrosion on steel.

Trial 3:

- 10 This trial demonstrates the stability of lithium glycerophosphate in a solution containing 1% concrete powder and 0.2% quickline. The stability of lithium glycerophosphate was compared during this trial with that of sodium monofluorophosphate. Figure 2 shows the  
15 curve of the concentrations of these two products as a function of time. The lithium glycerophosphate concentration remains almost stable, while that of the monofluorophosphate decreases very substantially over time.

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Trial 4:

- This trial demonstrates the capability of lithium glycerophosphate to penetrate a concrete structure. In particular, the penetrability of lithium  
25 glycerophosphate was compared during this trial with that of sodium monofluorophosphate. To carry out this trial, laboratory-manufactured mortar slabs were used. The lithium glycerophosphate concentration as a function of depth was measured by ion chromatography  
30 assay. Figure 3 shows the concentration of the products



in the slabs as a function of the depth. The results demonstrate the good penetrability of lithium glycerophosphate.

5    Trial 5:

This trial demonstrates the capability of the lithium element to significantly reduce the mobility of sulfates. A specimen of a concrete contaminated with an excess of sulfates was treated with lithium  
10    glycerophosphate and another specimen was untreated. After drying, these specimens were placed on blotting paper containing distilled water. The sulfate concentrations in the blotting papers after various extraction times were measured and plotted on the graph  
15    in figure 4. The results demonstrate the capacity of lithium to reduce the mobility of sulfates in concrete.

Trial 6:

Effects of lithium glycerophosphate on the environment  
20    (phytotoxicity).

Soybeans seeds were placed in an environment containing 0.2% lithium glycerophosphate. The soybean germination step - a crucial phase in its growth - was neither  
25    slowed down nor speeded up appreciably by this lithium glycerophosphate concentration.

According to the OCDE 302 B standard, lithium glycerophosphate is 100% biodegradable.

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Trial 7:

Effects of lithium glycerophosphate on building materials.

35    Test conditions:

Specimens of building materials were cleaned with alcohol. 500 µl of a 2 wt% lithium glycerophosphate solution (one drop) were pipetted onto the surface of the various specimens. After slow evaporation (over 3

to 4 hours) and 24 hours of reaction, the rest of the solution was removed, by simply rinsing with water.

All the following materials were shown to be inert  
5 (they did not react with the solution and no visible trace was noted after rinsing):

galvanized steel sheet; beige Jura limestone; tinplate;  
siliceous sandstone; copper; calcareous (Savonnière)  
sandstone; aluminum; black (Zimbabwe) granite; glass;  
10 marble (Carrera); PVC; stoneware (flagstones);  
unvarnished raw wood (beech).

Sole exception: the color of the oxidized copper was  
modified owing to the effect of cleaning with the  
15 solution. This phenomenon was not observed with  
oxidized zinc.

#### Trial 8:

Effect of lithium glycerophosphate on the compressive  
20 strength of concrete.

This trial measured the influence of adding a  
concentrated lithium glycerophosphate solution on the  
compressive strength of concrete cubes 7 days and 28  
25 days after production.

#### Description of the trial:

Several concrete test pieces of cubic shape (20 cm x  
20 cm x 20 cm) were produced from commercial concrete.  
30 An excess amount of water was intentionally added  
during manufacture, this being known to be deleterious  
to the compressive strength of the test pieces.

Five series of test pieces were manufactured using the  
35 same amounts of water. A first series contained no  
lithium glycerophosphate, a second series contained  
0.02% lithium glycerophosphate (relative to the weight  
of cement), a third series contained 0.05% lithium  
glycerophosphate (relative to the weight of cement), a

fourth series contained 0.13% lithium glycerophosphate (relative to the weight of cement) and the fifth series contained 0.24% lithium glycerophosphate (relative to the weight of cement).

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After the various species were matured and stored for 7 days and for 28 days, their compressive strengths were tested on a compression machine and their failure load measured.

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Observations:

It was observed (see the results shown in figures 5 and 6) that the addition of lithium glycerophosphate does not affect the compressive strength of the test pieces, whatever the lithium glycerophosphate concentration. From this it may be deduced that lithium glycerophosphate can be used to treat concrete structures without fear of it affecting its strength.

20 It was also noted that the addition of lithium glycerophosphate greatly increased the compressive strength of the species after 7 days and slightly increased it after 28 days. The graph of figure 6 shows the increases in strength of the various test pieces treated relative to the test pieces containing no lithium glycerophosphate.

This substantial increase in strength represents a certain advantage in the production of concrete structures. This is because, owing to this improved strength 7 days after production, successive concreting phases may be brought closer together in time. Thus, structures may be produced more rapidly and leveled more easily.

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Trial 9:

Influence of lithium glycerophosphate on the mobility of salts and on the capillary effect in concrete and the effect on steel rebars in this concrete.

Three concrete test pieces were produced using the same method as that used in the previous trial. Steel rebars were placed in these test pieces during their  
5 production. The dimensions of the test pieces were the following: height, 20 cm in the case of the first test piece and 15 cm in the case of the second and third test pieces; length, 20 cm; and depth, 9 cm.

10 The rebars were placed in the height direction and projected from the top of the test pieces.

The first test piece contained no lithium glycerophosphate.

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The second and third test pieces contained 0.24% lithium glycerophosphate (relative to the weight of cement) and 0.13% lithium glycerophosphate (relative to the weight of cement) respectively, the lithium  
20 glycerophosphate having been added to the cement paste before production of the test pieces.

After maturation of the test pieces for 17 days, they were immersed in a 3% sodium chloride solution up to  
25 one half of their height.

For 90 days, six phases of immersing the test pieces in the solution and five phases of drying the test pieces were alternated.

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Figures 7, 8 and 9 show the levels of capillary rise in the test pieces.

As indicated in figure 7, at the end of the last  
35 immersion phase, having lasted 3 days, it was noted that the solution had risen by capillary effect to the top of the test piece. In addition, the steel rebars started to show corrosion at the upper surface of the

test piece, this corrosion being due to the salts displaced by the capillary rise of the solution.

5 As indicated in figures 8 and 9, at the end of the last immersion phase, having lasted three days, it was noted that the solution did not rise up to the top of the test pieces. In addition, no onset of corrosion was observed on the steel rebars.

10 This trial shows that the presence of lithium glycerophosphate in the concrete has reduced the mobility of the ions, as was also described in trial 5.

15 This trial also shows the ability of the glycerophosphate to reduce the penetration of water into the concrete and, consequently, to reduce the amount of contaminants transported.